A superconductivity primer

Philip Campbell

High-temperature superconductors continue to tantalize the experts. Here is an introduction for others to both conventional and novel varieties.

SINCE the report a year or so ago, by J.G. Bednorz and K.A. Müller, that certain transition metal oxides are superconductors at unprecedentedly high temperatures, there has been a torrent of experimental and theoretical research aimed at defining the characteristics of these materials, understanding the mechanisms involved, and finding materials with transition temperatures even greater than the 95 K or so at which experimentalists now appear to be stuck. It was quickly realized that the theory of conventional superconductivity cannot account for the properties of the new materials. Whether an extension of present theories or a significantly new approach is necessary remains to be seen.

One remarkable feature of the past year has been the extent to which people from a variety of disciplines have been drawn into research in superconductivity. For that reason, not to mention the great interest that has been aroused among non-specialists, there may be a need for a summary in plain language of the basic attributes of conventional superconductors and the mechanisms involved, as well as the distinguishing features of the new materials.

What follows is not a formal review — no references are provided. The hope is simply that readers of this account may be better able to follow *Nature*'s past and future coverage of high-temperature superconductors and also next week's Boston meeting on the topic. A subsequent article will dwell on the distinctive characteristics of the new materials and the range of explanations being considered.

Electrical resistance

The most striking attribute of a superconductor is, of course, that its resistance to a direct current is zero, as far as can be measured. In one experiment, a current established in a superconducting ring was shown to have a decay time of not less than 100,000 years.

Seventy-five or so years after the discovery of superconductivity this 'perpetual motion' still seems hard to credit. After all, in a conventional conductor carrying a steady current, there is an equilibrium established between the force on the current-carrying electrons from the electric field and the resistance that they encounter arising from interactions with the atomic lattice. As it happens, a perfectly periodic and rigid lattice would provide no resistance at all because, in general, the scattering effects of neighbouring ions would destructively interfere and cancel. Resistance arises principally because thermal vibrations of the lattice and the presence of defects or impurities distort the regularity and give rise to net scattering.

Copper is a good example. Very pure copper crystals at liquid-helium temperature (4 K) have a conductivity nearly 100,000 times that measured at room temperature. The quantized lattice vibrations ('phonons') accounting for the enhanced resistance at higher temperatures individually scatter electrons and, indeed, can exchange energy and momentum with them. The stronger the electron–phonon interactions, the poorer the conductor.

Some of the electrical and thermal properties of ordinary conductors are well represented by the 'free electron' model, in which there is a sea of conduction electrons unaffected by the electric charges of the ionic lattice and scattered only rarely by each other. There is an infinity of states accessible to electrons, which are essentially those of the textbook quantum mechanics problem of an 'electron in a box'. At absolute zero (that is, in the ground state) the conduction electrons fill the lowest available energy levels up to a threshold known as the Fermi energy, E_F. As the temperature and thus the kinetic energy of the conduction electrons increase, higher levels become occupied at the expense of less energetic states.

The Fermi energy of metals is typically a hundred times larger than the average random thermal energy (kT, where k is Boltzmann's constant and T the temperature), so that only a small proportion of the electrons is raised in energy in this way, from just below to just above the Fermi energy level.

The free-electron theory provides a qualitative picture of conduction in the metallic state. In the ground state, the wave vectors of the electrons (solutions of the free-electron Schrödinger equation, encapsulating the electron distribution and behaviour) define a sphere in vector (momentum) space whose surface (defined by the maximum vector amplitude and corresponding to the Fermi energy) is called the Fermi surface.

The velocity of electrons at the Fermi surface is an important parameter: multiplied by the characteristic collision time, it gives the mean free electron path, which for copper is three millionths of a centimetre at room temperature and 0.3 cm at 4 K. Another important quantity is the number of different energy states per unit energy interval (the 'density of states') at the Fermi energy, which among other things is linked with the contribution by electrons to the specific heat of the metal.

While the free-electron model can account for many aspects of metallic behaviour, it does not explain why some materials are insulators and why others, the semiconductors, will conduct only when electrons acquire a minimum additional energy (as, for example, when the temperature is increased). But elaborations of this model which allow for the motion of the electrons in the periodic electric field of the lattice ions (the 'nearly-free-electron model'), show that in some crystal lattices, electrons of particular energies cannot propagate. This phenomenon underlies the existence of semiconductor 'band gaps', for example.

Electron–phonon interactions contribute to electrical resistance directly, but there are other ways in which the interaction between electrons and the lattice may affect the electrical properties of a metal. In particular, the mass of an electron may be effectively increased, both in metals and in insulators.

For example, in an ionic solid such as potassium chloride, an electron will interact repulsively with the chlorine anions and attractively with the potassium cations, thereby setting up a strain in the lattice. The combination of a local region of strain and the electron is referred to as a 'polaron'. The effect of these interactions is to increase the inertia and thus the effective mass of the electron. If the lattice strain is small (the case of the 'large polaron') the enhancement of mass is small and the electron moves freely within a conduction band. But the strain may be large ('small polaron'), in which case the electron will spend most of its time trapped by ions, tunnelling only slowly (or, at higher temperatures, hopping) through the lattice.

Superconducting metals

Two criteria must be satisfied if a material is to be classed as a superconductor: the electrical resistance to a direct current must be literally zero and the material must expel any external magnetic flux as it is cooled through its transition temperature in a magnetic field — the Meissner effect. The former of these two properties was that first recognized when, in 1911, H. Kamerlingh-Onnes examined the low-temperature properties of mercury. It took another 40 years or so for the effect to be fully explained.

Even before there was a satisfactory microscopic theory of superconductivity, it was clear that not all electrons in a superconductor are superconducting. The fraction of electrons conducting in a normal fashion increases gradually from zero at absolute zero to unity at the transition temperature. This explains why a superconductor, while exhibiting zero direct current (d.c.) resistance, does have a finite impedance to alternating currents.

The superconducting electrons which 'short circuit' a static electrical field must by some means be immune from the scattering by impurities and lattice vibrations which resist the movement of the ordinary electrons. A crucial clue to this mechanism was the discovery of the 'isotope effect': mercury specimens with different isotopic composition were found to have different superconducting transition temperatures varying (inversely) with the atomic mass, indicating that an electron–phonon interaction must be involved.

As it turns out, the infinite conductivity can be (and was historically) explained in two steps: (1) by demonstrating that it is a natural consequence of the 'superconductor energy gap' — a gap between the ground-state energy levels of the superconducting electrons and the minimum level to which they can be excited, and (2) by explaining the existence of such a gap in superconducting materials, as was finally achieved by J. Bardeen, L.N. Cooper and J.R. Schrieffer (BCS) in 1957.

For general understanding, the two steps are best inverted. BCS showed that, through the mediation of the electron–phonon interactions, there can be co-operative states of the system of all the electrons in a superconducting sample.

The cooperative states, being states of all the electrons, are not easily described except in terms of the simplified analysis due to L.N.Cooper (which preceded the full elaboration of BCS). First, electrons interact with the lattice which contains them through the Coulomb attraction of the ions, and thus also interact with phonons, the vibrational quanta of the lattice.

This process leads to an interaction between pairs of electrons which is distinct from but analogous to the electrostatic repulsion between them. In the language of quantum field theory, just as the electromagnetic interaction between two electrons is represented by the emission of a 'virtual' phonon by one and its absorption by the other, so the phonon interaction is represented by the emission and absorption of lattice phonons.

What are the forces that result? The calculations show that in suitable circumstances, the phonon-mediated forces between pairs of electrons can be attractive. One condition that must be satisfied for this to be the case is that the components of an electron pair must have opposite spins and equal and opposite momenta. The pair will be 'stable' so long as the electron thermal energy is less than the pair binding energy — a criterion that leads to an approximate determination of the critical temperature, at which these quantities are equal.

Cooper found that the spatial extent of such electron pairs might be of the order of 10^{-6} cm, much greater than the inter-ionic separation in the lattice. The strength of the coupling is determined by that of the electron–phonon interaction. This quantity determines electrical resistance in a normal metal, which explains why metallic superconductors are poor conductors above the superconducting transition temperature.

Plainly, the average energy (potential plus kinetic) of the superconducting electrons in a metal must be less than E_F — otherwise the cooperative state would not be formed. It turns out that the extra kinetic energy of the superconducting electrons is more than offset by their mutual binding energy due to electron–phonon coupling. BCS generalized Cooper's analysis for the 10^{23} 'free' electrons per cc that are found in a typical metal and thereby successfully demonstrated that such collective states can exist. For example, in a superconductor at absolute zero, when all the electrons are superconducting, they may be thought of as occupying the energy levels of a separate superconducting electron band with a maximum energy known as the 'superconductive ground-state energy', or E_0 for short, which lies below E_F.

BCS shows that superconducting electrons can be excited above E_0, but that the excited energy levels cannot fall below a certain minimum, which as it happens lies above the Fermi energy of the conventional metal. The gap separating the ground-state energy and this minimum is the 'energy gap' of a superconductor. (It should not be confused with the forbidden energy regions of semiconductors.)

As the temperature increases, this gap decreases, gradually at first and then rapidly to zero at the transition temperature. The gap manifests itself most obviously through the exponentially increasing specific heat of the material up to the discontinuity at the transition temperature as well as in the optical properties of superconductors.

One specific prediction of BCS is that the ground-state energy gap should be about 3.1 times the electron thermal energy at the transition temperature. The measurements of this ratio for high-temperature superconductors have proved troublesome, but all the signs are that it is significantly greater. The logic of BCS would imply that the pairing mechanism must involve stronger coupling than occurs in superconducting metals.

What happens if a steady current is established in a loop of superconductor in its ground state? The maximum energy level is now slightly increased because of the extra kinetic energy, but the entire population of superconducting electrons still fills the available states at or below that threshold. For one of those electrons to achieve a different state after scattering by a phonon, for example, it must bridge the energy gap. But there is insufficient energy available, so that the scattering cannot occur, with the consequence that the material offers no electrical resistance.

Two aspects of the BCS explanation of metallic superconductivity highlight the difficulties of visualizing the mechanisms involved. First, the electrons cannot be described as distinct point-like entities in space but, as described by the quantum mechanical formalism of BCS, are 'delocalized'. Second, it is the momentum characteristics of electrons as mentioned above, not their physical location, that determines pair formation. For this reason, the BCS interactions can be described as 'momentum-space' pairing.

In contrast, some of the pairing mechanisms suggested for the new oxide superconductors arise in 'real space'. Be that as it may, it turns out that the collective behaviour of an ensemble of paired electrons can most conveniently be described by a single many-particle 'macroscopic' wave-function. As will be seen, it is this aspect of superconducting electron behaviour that readily accounts for some of the most striking characteristics of superconducting devices.

The BCS treatment thus provides an explanation of zero resistance. It also quantifies the maximum current, in principle, that a superconductor can carry without losing its superconducting properties: the additional kinetic energy of electrons carrying a current can reach the point at which it exceeds that required to break the 'Cooper' pairs. In practice the critical currents of superconductors are smaller, sometimes by many orders of magnitude, than this limit because their magnetic side-effects are also detrimental to superconductivity.

Subsequent work has shown that, for all its power, BCS cannot explain some of the fine detail of metallic superconducting behaviour because it assumes instantaneous pairings. But the phonons generated by an individual electron travel maybe hundreds of times more slowly than the 10^6 m s^{-1} (the 'Fermi velocity') of typical electrons. The pairing interaction (first quantified in its time-retarded form by Eliashberg) is thus sometimes depicted in terms of messages left by electrons for one another in the form of lattice polarization.

It is too early to tell, but one of the crucial differences between the metallic and the new oxide superconductors may be that the pairing mechanism for the latter is effectively instantaneous. Certainly, most theorists have concluded that the BCS mechanism can, at most, represent only a small contributing factor at superconducting temperatures above 40 K. But several unique aspects of these materials — their anisotropic structure and the apparently crucial influence of oxidation state are but two — severely complicate the lives of those attempting to elucidate the underlying processes.

Magnetic behaviour

The response of a superconductor to external magnetic fields most vividly illustrates how far removed from classical electromagnetism are the underlying processes. For a 'conventional' conductor, the bulk magnetic behaviour can be predicted using Maxwell's equations, with the additional constraints provided by Ohm's law, to show that, as a sample undergoes a transition to zero resistance, the internal magnetic field will be trapped.

The fact that a superconductor, by contrast, expels the field implies that the standard picture of a sea of conduction electrons is inappropriate. The underlying reason for the characteristic behaviour of superconductors is that the wave-functions of the superconducting states in effect describe ensembles of pairs of electrons with opposite spins which, as entities, are not restricted by the Pauli exclusion principle that no two may be in exactly the same state. The consequence is that the superconducting electrons within a sample in a static magnetic field will respond by forming a pattern of surface currents which actually cancels out the external field. That this would happen was surmised long before BCS by F. and H. London in 1935.

This behaviour has been called 'perfect diamagnetism', but it differs from conventional diamagnetism in that macroscopic surface currents, rather than changes of atomic magnetic moments, are its driving force. The Londons' analysis showed that the field decays exponentially into the sample over a characteristic 'penetration depth', λ, typically for metals between 10 and 100 nm.

The Londons' simple description was found by A.B. Pippard to be insufficient to account for the way in which the penetration length for a pure superconducting metal (tin) depends on the orientation of the surface relative to the (tetragonal) crystal axes. He showed that the current flowing at any particular point would be a function of the magnetic field within a certain distance of that point, called the 'coherence length'. The London equations, in contrast, relate the current to the magnetic field only at the point itself. (More precisely, the London and Pippard equations relate the current density to the magnetic vector potential.) As will be seen, the coherence length is a crucial characteristic of any superconducting material.

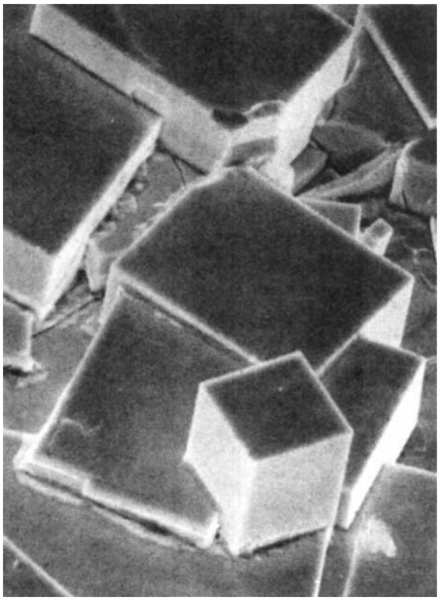
There are two types of superconductor, distinguished by their response to an applied magnetic field. Type I superconductors exhibit perfect diamagnetism up to a critical applied field, at which point the superconductivity is lost and the average magnetization of a sample rises abruptly from −1 to the value (near zero) of the normal material. (The abruptness depends to some extent on the shape of the sample, the ideal transition occurring for a thin rod or wire.) In type II materials the magnetization is governed by two critical values of the applied field; from −1 at the lower threshold it gradually increases, only reaching the normal value at the upper critical field, which in some cases is one hundred times stronger than the lower. Between the two thresholds (the 'mixed' state), magnetic flux penetrates the sample in discrete threads and superconductivity persists.

Typical values of critical fields for type I superconductors (for example pure metals) lie roughly between 0.01 and 0.1 tesla. The value quoted applies to absolute zero, the critical field decreasing to zero as the temperature is raised to the transition value. Type II superconductors (which, apart from vanadium and niobium, are alloys and compounds) have lower critical field intensities similar to the type I values above, whereas the upper critical field strength may amount to several teslas or more.

The new oxide superconductors are type II materials with upper critical fields typically greater than 100 teslas. Their anisotropic structures combined with the difficulties of producing superconducting single crystals have so far rendered it impossible to achieve a consensus as to values of penetration depths or coherence lengths.

Phase transitions

As far as conventional superconductors are concerned, the BCS theory can explain all these phenomena and more, but considerable insight was obtained in advance of that by Ginzburg and Landau who, in 1950, analysed the energetics of the superconducting phase changes. Landau had previously produced a general theory of second-order phase transitions (in which the entire system changes state essentially simultaneously without the involvement of latent heat). The essential concept of Landau's theory is the 'order parameter', having its maximum magnitude when the system is most ordered (a lattice of parallel atomic dipoles in a magnet for example), as might



Crystals of superconducting $YBa_2Cu_3O_7$. Most samples of high-temperature superconductors have been polycrystalline, and the resulting presence of grain boundaries has hampered investigations (see text). Fractionation during solidification of molten oxides hinders the growth of large single crystals of superconductors. The crystal shapes seen above reflect the orthorhombic crystal structure.

occur at absolute zero. As temperature increases, the order parameter decreases, becoming zero (maximum disorder) at and above the critical temperature. To explain phenomena in the neighbourhood of the transition, Landau formalized the free-energy density of the system in terms of the order parameter and thus determined the value of the parameter associated with the minimum free energy at a given temperature.

Ginzburg and Landau applied this theory to superconductors. The condition for a minimum of free energy, it turns out, closely resembles a Schrödinger equation, thus allowing the identification of the order parameter with the macroscopic wave-function mentioned above. The solutions reveal several features of superconductors: they reproduce the London/Pippard equations; they yield a characteristic minimum length over which the wave-function can significantly change — the coherence length; and they show that the wave-function will extend out of the superconductor at a boundary — in other words, electron pairs can tunnel out of the superconductor in certain circumstances. This phenomenon is crucial to the Josephson effect (see below) which underlies so many applications of superconductors.

Perhaps the most significant insight provided by the Ginzburg–Landau theory concerns the difference between type I and type II superconductors as exhibited in their contrasting responses to external magnetic fields. The expulsion of magnetic flux by a sample costs energy, and there will clearly be an applied field strength at which it becomes energetically easier to assume the normal conducting state.

Loosely speaking, Ginzburg and Landau showed that if — as in type II materials — the penetration depth exceeds the coherence length, the increase in energy of the bulk from the formation of restricted regions of normal conducting material is more than offset by the decrease in magnetic energy as the flux enters those regions. Thus normal 'cores' are formed, lying parallel to the applied field, sheathed by vortices of supercurrent and threaded by magnetic flux.

It turns out that a triangular lattice of cores is the preferred geometry in this mixed state. At the lower critical field the normal cores are spaced a penetration depth apart. As the field increases, more cores are formed and the separation decreases until, at the upper critical field, the cores are separated only by a coherence length or so.

This 'vortex motion' can be inhibited if there are impurities or defects such as grain boundaries present. As the field increases above the lower critical threshold, such 'flux pinning' (which is yet to be fully explained at the microscopic level) inhibits the inward motion of newly formed cores, thus generating a magnetic-field gradient within the material boundary which must, by Maxwell's equations, be associated with an enhanced current flow. Thus control of microstructure can allow one to engineer materials of comparatively high critical currents, with clear practical benefits.

The inhibition of homogenous flux penetration by pinning renders the upper critical field transition irreversible — thence the terminology 'reversible' and 'irreversible' type II materials.

Flux quantization

The macroscopic wave-function that describes the superconducting state has a clearly defined phase and amplitude. An analysis of its behaviour in a superconducting loop shows that the magnetic flux that can thread the loop is quantized. The quantum units ('fluxoids') have a value $h/(2e) \approx 2.10^{-15}$ T m^2, where h is Planck's constant and e is the electronic charge. The appearance of $2e$ as the denominator reflects the electron pairing involved. It was a flux quantization experiment of this sort that confirmed that some type of electron pairing underlies the behaviour of the new high-temperature superconductors.

Josephson effects

If two superconductors are separated by a sufficiently thin layer of insulator (two metal layers separated by an oxide, for example), the penetration of the barrier by the macroscopic wave-functions leads to overlap, or electron-pair tunnelling, the effects of which were quantified by Brian Josephson in 1962. He showed that if there is a phase difference between the two wave-functions then a current will flow in the absence of any potential difference.

An insulating layer is not the only possible type of 'weak link', others being a finely ground point contact between the two superconductors or a microbridge formed by etching a superconducting thin film. In practice, a current can be fed at zero voltage through the junction up to a threshold value above which a voltage appears across the junction. The voltage then increases with increasing current. This phenomenon is known as the 'd.c. Josephson effect'. The 'a.c.' effect occurs when a voltage is applied across the junction and oscillatory currents are found to flow.

As will be seen, the Josephson effect permits many applications. But it can also be an irritant. It arises at grain boundaries within polycrystalline samples of the new oxide superconductors and, for example, hinders attempts to measure London penetration depths.

Materials

Of the chemical elements, only non-magnetic metals are found to superconduct, and none of them has a critical temperature greater than 10 K. The addition of impurities generally has little effect on the transition temperatures but, as we have seen, may drastically affect the magnetic and current-carrying properties. Metallic compounds may also be superconducting, and those compounds of vanadium and niobium with the cubic β-W(A15) structure are found to be particularly prone. These had the highest critical temperatures (up to 23 K) before the new oxide variety was discovered. The highest critical fields, on the other hand, were associated with the 'Chevrel phase' compounds with the general formula $M\,Mo_6X_8$. Mention should also be made of 'exotic' species such as organic and heavy-electron superconductors. As with the oxide materials, their mechanisms are not well understood.

Applications

Computers. Josephson junctions offer the capacity to switch ten times faster than semiconducting circuits, with energy losses several orders of magnitude smaller. The latter aspect clearly allows much higher packing density.

Logic circuits exploit the transition between a zero and a finite voltage at a particular current threshold. A Josephson junction is put in parallel with a resistive circuit and couple to three control lines. Depending on the combination of signals in the control lines, a voltage may or may not be generated in the resistance. Thus AND, OR and other logic arithmetic can be achieved.

Memory circuits exploit the capacity of two junctions in a loop to carry persistent currents in the absence of an applied voltage, in switchable clockwise or anticlockwise directions that can be made to correspond to the values 1 or 0.

Microwave and sub-millimetre detectors. These use the highly nonlinear current–voltage relationship of Josephson junctions to mix the output of a local oscillator with an incoming signal, as in a standard heterodyne receiver, to produce a signal at an intermediate frequency. If the oscillator current flowing through the junction has a frequency only slightly different from that of the much weaker signal, the resulting current will be amplitude-modulated by an amount proportional to the signal amplitude.

SQUIDs (superconducting quantum interference devices). These devices provide the most sensitive instruments available for the measurement of magnetic fields, magnetic susceptibilities and voltages. The d.c. SQUID consists of a superconducting ring containing two Josephson junctions. A current which exceeds the zero-voltage threshold of both junctions is pulsed from one side of the ring to the other. Due to quantum interference between macroscopic wave-functions, an imposed magnetic field will change the voltage generated to an extent that is periodic with the field strength, with one cycle per fluxoid, allowing exceedingly sensitive detection (changes of 10^{-11} teslas with a 1-cm ring). A radio frequency (r.f.) SQUID consists of a ring with a single junction coupled to a tuned r.f. circuit. Both d.c. and r.f. SQUIDs have been constructed with high-temperature materials, exploiting their granularity to provide intrinsic Josephson junctions.

Magnets. Superconductors enable magnetic fields to be generated with zero dissipation and, indeed, are now routinely used when very high fields are required. Desirable characteristics of the material are a high transition temperature (which ensures a high upper critical field), high normal-state resistivity (which leads to a large penetration depth compared to the coherence length, and which in turn ensures a higher upper critical field), and high disorder to enhance flux pinning and hence increase the critical currents. Such high-resistance material has the disadvantage of generating heat if it becomes normally conducting, so windings are usually clad in copper to provide a shunt. Unfortunately, the advantages of high critical fields are, for some metal compounds, offset by their brittleness. This also happens to be but one of the several problems that has impeded the use of the high-temperature superconductors. □

Philip Campbell is Physical Sciences Editor of Nature.